ESR Studies of the Copper(II) Complexes of Amino Acids

Hiroshi Yokoi, Mitsuru Sai, Taro Isobe, and Shigeru Ohsawa*

Chemical Research Institute of Non-aqueous Solutions, Tohoku University, Katahira, Sendai

**Department of Chemistry, Faculty of Science, Tohoku University, Katahira, Sendai*

(Received February 2, 1972)

The X-band and K-band ESR spectra of the *trans*-planar copper(II) complexes of amino acids, whose crystal structures are now known, were measured in a polycrystalline state at room temperature and in frozen aqueous-methanolic solutions at the temperature of liquid nitrogen. The polycrystalline samples showed a variety of ESR line shapes, most of which had three different principal g values; $g_1=2.04$—2.07, $g_2=2.08$—2.12, and $g_3=2.16$—2.29. On the other hand, all the ESR line shapes observed for the frozen solutions were quite similar, and they indicate a normal tetragonal copper(II)-ion environment. There was, moreover, a remarkable difference in the g values between the complexes in the two states. The correlation among the g values, the *d-d* band energies, the bonding parameters (a measure of the degree of covalency of the copper-ligand bondings), and the geometrical configurations of the coordinating atoms for the complexes in a crystal is discussed in some detail.

ESR studies of metal complexes present much useful information about coordination bonding.[1-11] It is very important to see how the ESR data correlate practically with various structural factors for the metal complexes with complicated structures. Recently, some works along this line have been reported; the optical absorption and ESR studies of various ammine and ethylenediamine complexes of copper(II) whose crystal structures are known were carried out in the form of single crystals or of polycrystals, and rhombic g tensors have been discussed in terms of a ground-state of the form: $\varphi=a|x^2-y^2\rangle-b|z^2\rangle$.[6,12-14]

The metal complexes of amino acids have structures likely to participate in hydrogen-bonding with their surroundings, and any of their crystal structures is unpredictably unique because of their characteristic hydrogen-bonding behavior.[15,16] The purpose of this paper is to present the ESR spectra of the copper(II) complexes of amino acids, whose crystal structures are known, in the form of polycrystals and in frozen aqueous-methanolic solutions, and to investigate the ESR and optical absorption data in connection with the structures. This kind of investigation seems to be fundamentally important for the structural estimation of various other metal complexes and the metal-binding sites of various metalloenzymes.[17]

Experimental

Materials. The samples employed here are listed in Table 1, together with their abbreviations. The amino acids used were all commercial products except for cyclopentane-1-amino-1-carboxylic acid, which was prepared and purified according to the method of Henze and Speer.[18] The copper(II) complexes of these amino acids were prepared by the usual method,[19,20] and were recrystallized from water. The results of the chemical analyses are also listed in Table 1.

Measurements. The X-band and K-band first-derivative ESR spectra were measured for the powdered samples at room temperature and for the frozen solutions at the temperature of liquid nitrogen with a Hitachi ESR spectrometer, Model MES-4001. The sample solutions were in concentrations of 10^{-3}—10^{-4}M of the complexes, with an equivolume mixture of water and methanol used as the solvent. The field was calibrated with an Oki magneto-field scope, Model WX-601, using the NMR signals of proton and lithium, and then with a benzene solution of vanadyl acetylacetonate. The visible absorption spectra were measured for the powdered samples at room temperature with a Cary model 14 spectrometer, using the so-called opal-glass method, where a suspension of finely-powdered samples in

1) A. Abragam and M. H. L. Pryce, *Proc. Roy. Soc., Ser. A*, **205**, 135 (1951).
2) K. W. H. Stevens, *ibid., Ser. A*, **219**, 542 (1953); J. Owen, *ibid., Ser. A*, **227**, 183 (1955).
3) A. Abragam and B. Bleaney, "Electron Paramagnetic Resonance of Transition Ions," Clarendon Press, Oxford (1970).
4) B. R. McGarvey, "Transition Metal Chemistry," Vol. 3, ed. by R. L. Carlin, Marcel Dekker, New York (1967), p. 89.
5) S. Fujiwara, "Spectroscopy and Structure of Metal Chelate Compounds," ed. by K. Nakamoto and P. J. McCarthy, John Wiley & Sons, New York (1968), p. 286.
6) J. Hathaway and D. E. Billing, *Coordin. Chem. Rev.*, **5**, 143 (1970).
7) B. G. Malmstrom and T. Vånngård, *J. Mol. Biol.*, **2**, 118 (1960).
8) A. H. Maki and B. R. McGravey, *J. Chem. Phys.*, **29**, 31, 35 (1958).
9) D. Kivelson and R. Neiman, *ibid.*, **35**, 149 (1961).
10) H. Yokoi and T. Isobe, This Bulletin, **41**, 2835 (1968); *ibid.*, **42**, 2187 (1969).
11) H. Yokoi, M. Sai, and T. Isobe, *ibid.*, **42**, 2232 (1969); *ibid.*, **43**, 1078 (1970).
12) I. M. Procter, B. J. Hathaway, and P. Nicholls, *J. Chem. Soc., A*, **1968**, 1678.
13) A. A. G. Tomlinson, B. J. Hathaway, D. E. Billing, and P. Nicholls, *ibid.*, **1969**, 65; B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *ibid.*, **1969**, 312, 319.
14) M. A. Hitchman, C. D. Olson, and R. L. Belford, *J. Chem. Phys.*, **50**, 1195 (1969); M. H. Hitchman, *J. Chem. Soc. A*, **1970**, 4.
15) H. C. Freeman, "The Biochemistry of Copper," ed. by J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York (1966), p. 77.
16) W. E. Hatfield and R. Whyman, "Transition Metal Chemistry," ed. by R. L. Carlin, Vol. 5, Marcel Dekker, New York (1969), p. 47.
17) J. Peisach and W. E. Blumberg, "Electron Spin Resonance of Metal Complexes," ed. by T. F. Yen, Plenum Press, New York (1969), p. 71, and the references therein.
18) H. R. Henze and R. J. Speer, *J. Amer. Chem. Soc.*, **64**, 522 (1942).
19) E. Abderhalden and E. Schnitzler, *Z. Physiol. Chem.*, **163**, 94 (1927).
20) D. P. Graddon and L. Munday, *J. Inorg. Nucl. Chem.*, **23**, 231 (1961).

Table 1. Sample complexes and chemical analyses

Ligand (Abbreviation of the anion of ligand)	Copper(II) complex	C, %		H, %		N, %	
		Found	Calcd	Found	Calcd	Found	Calcd
L-Alanine (L-Ala)	$[Cu(L\text{-}Ala)_2]$	30.34	30.06	4.91	5.05	11.85	11.68
DL-α-Amino-*n*-butyric acid (DL-α-NH_2but)	$[Cu(DL\text{-}\alpha\text{-}NH_2but_2)]$	35.97	35.88	5.73	6.02	10.50	10.46
DL-Methionine (DL-Met)	$[Cu(DL\text{-}Met)_2]$	33.45	33.37	5.39	5.60	7.90	7.78
DL-Valine (DL-Val)	$[Cu(DL\text{-}Val)_2]$	40.73	40.60	6.52	6.82	9.56	9.47
DL-Serine (DL-Ser)	$[Cu(DL\text{-}Ser)_2]$	26.80	26.52	4.40	4.45	10.52	10.31
Cyclopentane-1-amino-1-carboxylic acid (Pen)	$[Cu(Pen)_2]$	44.98	45.06	6.05	6.30	8.86	8.76
DL-Proline (DL-Pro)	$[Cu(DL\text{-}Pro)_2]\cdot 2H_2O$	36.76	36.64	6.42	6.16	8.69	8.55
L-Proline (L-Pro)	$[Cu(L\text{-}Pro)_2]\cdot 2H_2O$	36.35	36.64	5.98	6.16	8.37	8.55
β-Alanine (β-Ala)	$[Cu(\beta\text{-}Ala)_2]\cdot 6H_2O$	21.13	20.72	6.65	6.96	8.31	8.06
β-Amino-*n*-butyric acid (β-NH_2but)	$[Cu(\beta\text{-}NH_2but)_2]\cdot 2H_2O$	31.42	31.63	6.62	6.64	9.41	9.22
L-Glutamic acid (L-Glu)	$Cu(L\text{-}Glu)\cdot 2H_2O$	24.13	24.54	4.49	4.53	5.67	5.72

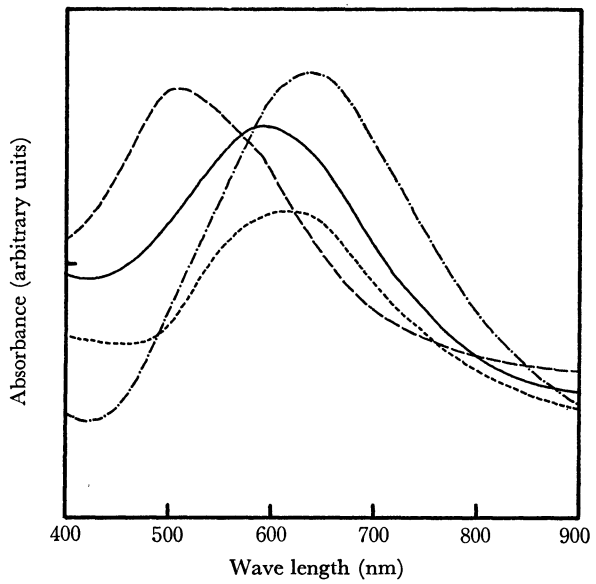

Fig. 1. Visible absorption spectra in a polycrystalline state.
——: $[Cu(L\text{-}Ala)_2]$, ——: $[Cu(Pen)_2]$,
------: $[Cu(DL\text{-}Pro)_2]\cdot 2H_2O$, -·-·-: $[Cu(\beta\text{-}Ala)_2]\cdot 6H_2O$.

liquid paraffin is dealt with;[21] several of the observed spectra are shown in Fig. 1.

Results and Discussion

Principal Values of g. The observed powder ESR spectra, which are shown in Figs. 2—5, were analyzed by the use of the approximation of Kneubühl;[22] the results are shown in Table 2.

The principal values of g for the copper(II) ion in a rhombic field, for which the ground-state may be written as in Eq. (1),

$$\varphi=\cos\delta(d_{x^2-y^2})-\sin\delta\,(d_{z^2}) \qquad (1)$$

can generally be given by the following expressions;[6,14,23,24]

$$g_x=2-\frac{2k_x^2\lambda}{\Delta E_{xz}}(\sqrt{3}\,\sin\delta-\cos\delta)^2$$
$$g_y=2-\frac{2k_y^2\lambda}{\Delta E_{yz}}(\sqrt{3}\,\sin\delta+\cos\delta)^2 \qquad (2)$$

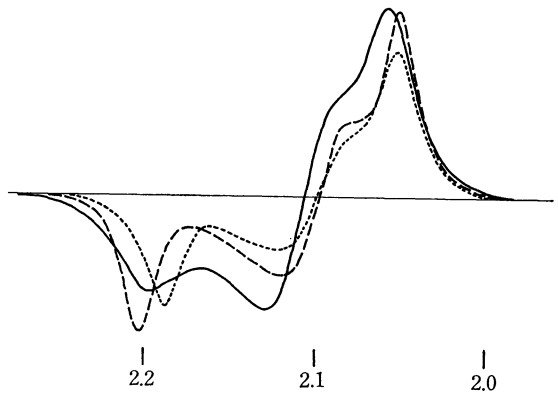

Fig. 2. Powder K-band ESR spectra at room temperature (the numbers represent g values).
——:$[Cu(L\text{-}Ala)_2]$, -----:$[Cu(DL\text{-}\alpha\text{-}NH_2but)_2]$,
------:$[Cu(DL\text{-}Met)_2]$.

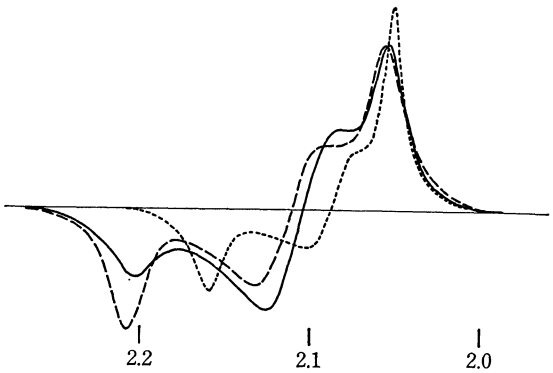

Fig. 3. Powder K-band ESR spectra at room temperature (the numbers represnt g values).
——:$[Cu(DL\text{-}Val)_2]$, -----:$[Cu(DL\text{-}Ser)_2]$,
------:$[Cu(Pen)_2]$.

21) K. Shibata, "Jikken Kagaku Koza," Vol. 11, ed. by Chem. Soc. Japan, Maruzen, Tokyo (1965), p. 192; "Methods of Biochemical Analysis," Vol. 7, ed. by D. Glick, Interscience Publ., New York (1959), p. 77; *ibid.*, Vol. 9 (1962), p. 217.
22) F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).
23) B. Bleaney, K. D. Bowers, and M. H. L. Pryce, *Proc. Roy. Soc. Ser. A*, **228**, 166 (1955).
24) G. F. Kokoszka, H. C. Allen, and G. Gordon, *J. Chem. Phys.*, **42**, 3693 (1965).

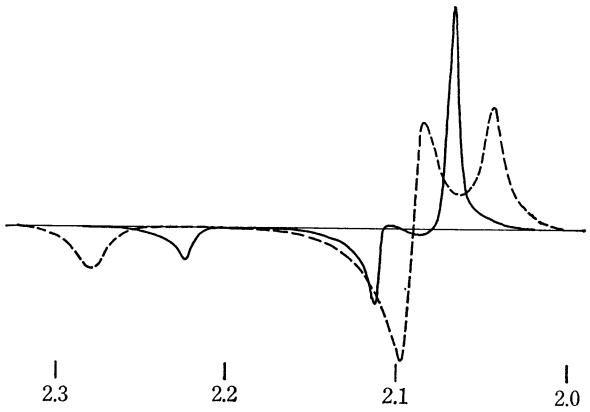

Fig. 4. Powder K-band ESR spectra at room temperature (the numbers represent g values).
——:[Cu(β-Ala)$_2$]·6H$_2$O, ------:[Cu(β-NH$_2$but)$_2$]·2H$_2$O.

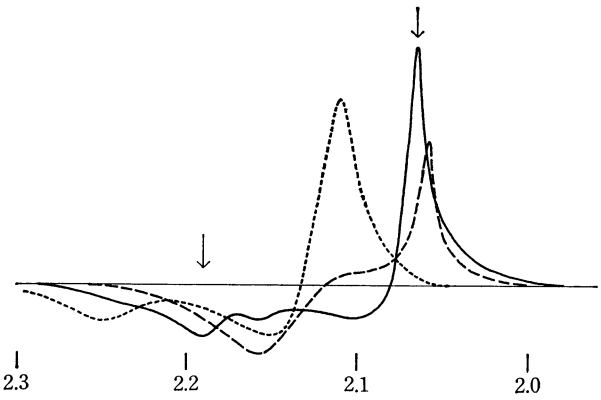

Fig. 5. Powder K-band ESR spectra at room temperature (the numbers represent g values).
——:[Cu(DL–Pro)$_2$]·2H$_2$O, -----:[Cu(L–Pro)$_2$]·2H$_2$O, ------:Cu(L–Glu)·2H$_2$O.

TABLE 2. g VALUES AND VISIBLE ABSORPTIONS IN A POLYCRYSTALLINE STATE

Copper(II) complex	g_1	g_2	g_3	λ_{max} (nm)
[Cu(L-Ala)$_2$]	2.059	2.107	2.197	590
[Cu(DL-α-NH$_2$but)$_2$]	2.052	2.098	2.204	585
[Cu(DL-Met)$_2$]	2.053	2.100	2.190	580
[Cu(DL-Val)$_2$]	2.057	2.105	2.202	605
[Cu(DL-Ser)$_2$]	2.058	2.112	2.208	615
[Cu(Pen)$_2$]	2.053	2.089	2.160	490, 590[a]
[Cu(DL-Pro)$_2$]·2H$_2$O[b]	(2.065)[c]		(2.190)	605
[Cu(L-Pro)$_2$]·2H$_2$O	2.058	2.158[c]		610
[Cu(β-Ala)$_2$]·6H$_2$O	2.068	2.109	2.223	635
[Cu(β-NH$_2$but)$_2$]·2H$_2$O	2.044	2.090	2.280	655
Cu(L-Glu)·2H$_2$O	2.111[c]		2.250	720

a) These values were roughly estimated by a Gaussian analysis.
b) The g values were tentatively determied from the positions shown by arrows in Fig. 5.
c) The numbers written between the neighboring g columns express the same g values in both of the columns.

$$g_z = 2 - \frac{8k_z^2\lambda}{\Delta E_{xy}}(\cos\delta)^2$$

where k^2s are the orbital reduction factors, which are regarded as an approximate measure of the degree of covalency for the coordinate bonds of planar copper(II) complexes,[2,5,25] and where the other symbols have their usual meanings. In Eqs. (1) and (2), the normal tetragonal copper(II)-ion environment with which we have most often met means $\cos\delta=1$. It is clear from Eq. (2) that the inclusion of a small amount of a d_z^2 character in the ground-state is sufficient to account for the fairly large difference between the g_x and g_y values. On the assumption of a square-planar configuration to start with, none of the small distortions except for a rhombic or rectangular one is important in affecting the g values and the d-d band energies.[26] g_x, g_y, and g_z can now be assumed to correspond to g_1, g_2, and g_3 respectively in Table 2.

Before discussing the g values directly determined from the powder ESR spectra, it is necessary to check whether these g values reflect the local copper(II)-ion environment. If a large spin-exchange interaction is present between crystallographically non-equivalent molecules, the determined g values will not be equal to the principal g values of the local copper(II) ions. Hathaway *et al.* defined the value of $(g_{//}-2)/(g_{\perp}-2)$ as G and used this G value as a criterion for examining whether there is such a strong spin-exchange interaction in a crystal; when $G<4$, such a strong interaction is considered to be present.[5,12] Much reliance, however, can not always be placed on this criterion, since many planar copper(II) complexes have been known to have $G<4$ even in the magnetically-diluted state,[9,27] and since there is always a possibility that $G<4$ can be established for certain planar copper(II) complexes because of the unusual order of the d-orbital levels or of the bonding parameters.

The results of the X-ray analysis of all the copper(II) complexes of amino acids whose crystal structures are known are listed in Table 3. A spin-exchange interaction between crystallographically-equivalent molecules makes the ESR absorption line widths decrease, but does not change the g values; in such a case, the determined g values directly reflect the local copper(II)-ion environment. The three different g values clearly observed for [Cu(β-NH$_2$but)$_2$]·2H$_2$O are, accordingly, just its true principal g values, since this complex has one molecule per unit cell.[34] Similarly, all the other complexes in Table 3 except [Cu(DL-Pro)$_2$]·2H$_2$O and Cu(L-Glu)·2H$_2$O have three different g values in spite of their having two molecules per unit cell. Evidently the first four complexes in Table 3, which have no water molecules in the crystal, are significantly different in the relative configurations of the two crystallographically non-equivalent molecules in an unit cell. Nevertheless, these four complexes are quite similar in ESR line shape, as is shown in Figs. 2 and 3. This suggests that there may be no such strong spin-exchange interactions as has been mentioned above in most crystals of the copper(II) complexes of amino acids. This is also

25) M. Gerloch and J. R. Miller, *Progr. Inorg. Chem.*, **10**, 1 (1968).
26) W. E. Blumberg, "The Biochemistry of Copper," ed. by J. Peisach, P. Aisen, and W. E. Blumberg, Academic Press, New York (1966), p. 49.
27) A. K. Wiersema and J. J. Windle, *J. Phys. Chem.*, **68**, 3216 (1964); S. E. Harrison and J. M. Assour, *J. Chem. Phys.*, **40**, 365 (1964); T. Chiang, *ibid.*, **48**, 1814 (1968).

Table 3. X-ray crystallographic data

Copper(II) complex	Space group	Z	L_N Cu–N distance (Å)	L_O Cu–O distance (Å)	L_A[a] Cu–O(apical) distance (Å)	θ ∠N–Cu–O (deg.)	Ref.
[Cu(L-Ala)$_2$]	$P2_1$	2	2.01—2.02	1.96—1.97	2.70 (carboxyl) 2.90 (carboxyl)	87	28
[Cu(DL-α-NH$_2$but)$_2$]	$P2_1/c$	2	2.02	1.98			29
[Cu(DL-Met)$_2$]	$P2_1/a$	2	1.98	1.95	2.71 (carboxyl)	84	30
[Cu(Pen)$_2$]	$P2_1/a$	2	1.98	1.91	3.17 (carboxyl)	85	31
[Cu(DL-Pro)$_2$]·2H$_2$O	$P2_1/n$	2	1.99	2.03	2.52 (water)	82	32
[Cu(β-Ala)$_2$]·6H$_2$O	$P2_1/c$	2	2.04	2.01	2.53 (water)	91	33
[Cu(β-NH$_2$but)$_2$]·2H$_2$O	P_1	1	1.99	2.00	2.45 (waer)	92	34
Cu(L-Glu)·2H$_2$O[b]	$P2_12_12_1$	4	2.00	1.97	2.3 (carboxyl) 2.6	84	35

a) The apical oxygen atoms belong to the groups shown in parentheses.
b) The square planar coordination of this complex is due to two oxygen atoms and a nitrogen atom of glutamates and one oxygen atom of a water molecule.

supported by other ESR experiments concerning the aggregation and dimerization of the complexes in frozen aqueous media.[36] Therefore, it may be concluded that almost all the g values determined here are correct as principal g values.

Correlation Between g *Values and Crystal Structures.* The *trans*-planar copper(II) complexes of amino acids are mainly dealt with in this work. The coordination about the copper atom is schematically represented in Fig. 6, where O_{A1} and O_{A2} are the double-bonded oxygen atoms of adjacent molecules for some complexes, or the oxygen atoms of water molecules for other complexes.

[Cu(L-Ala)$_2$] showed a typical powder ESR spectrum, with relatively broad absorption lines and three different g values. Many other copper(II) complexes of amino acids, such as [Cu(DL-α-NH$_2$but)$_2$], [Cu(DL-Met)$_2$], [Cu(DL-Val)$_2$], [Cu(DL-Ser)$_2$], and [Cu(Pen)$_2$], showed similar powder ESR line shapes, as may be seen in Figs. 2 and 3. [Cu(Pen)$_2$] is characterized by the smallest g_3 value. On the other hand, [Cu(β-Ala)$_2$]·6H$_2$O and [Cu(β-NH$_2$but)$_2$]·2H$_2$O showed comparatively sharp absorption lines, as Fig. 4 shows, and they had large g_3 values compared with all the other complexes. Cu(L-Glu)·2H$_2$O also had large g values. It has been a generally-accepted rule that the g values decrease as the planar ligand field becomes stronger, or as the axial ligand field becomes weaker,[4,11,37] and that this behavior of the ligand field is accompanied by a blue-shift of the *d-d* absorption bands.[38] The above-mentioned characteristics of the g values for [Cu(Pen)$_2$], *etc.* can be understood from their structures and observed visible absorptions according to this general rule. [Cu(Pen)$_2$] has an especially large L_A value and relatively small L_N and L_O values, and its visible absorption appears at shorter wavelengths, as Tables 2 and 3 show. [Cu(β-Ala)$_2$]·6H$_2$O and [Cu(β-NH$_2$but)$_2$]·2H$_2$O have comparatively large L_N and L_O values and small L_A values, and their visible absorptions appear at longer wavelengths. Cu(L-Glu)·2H$_2$O, which showed a visible absorption at the longest wavelength, has an especially small L_A value.

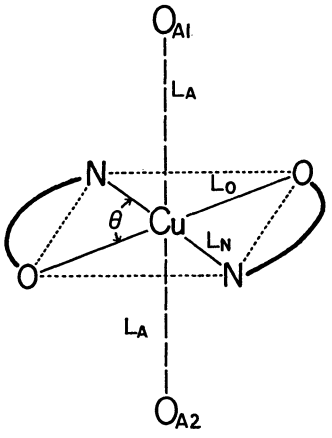

Fig. 6. The schematically represented structure of the *trans*-planar copper(II) complexes of amino acids.

It has generally been believed that the g_3 (or g_z) is oriented along the axis normal to the molecular plane and that the g_1 and g_2 (or g_x and g_y) axes lie on the plane;[34,39] moreover, in view of the crystal-field theory, it is a most probable assumption that the g_1 and g_2 axes are nearly oriented along the different respective coordinate bond directions. All the complexes employed here except three have three different principal values of g. This fact indicates that the copper(II) ions of these complexes are present in rhombically-distorted ligand fields. However, the differences between the g_1 and g_2 values were almost constant for

28) A. Dijkstra, *Acta Crystallogr.*, **20**, 588 (1966).
29) A. J. Stosick, *J. Amer. Chem. Soc.*, **67**, 362 (1945).
30) M. V. Veidis and G. J. Palenik, *Chem. Commun.*, **1969**, 1277.
31) C. A. Barclay and F. S. Stephens, *J. Chem. Soc.*, **1963**, 2027.
32) A. McL. Mathieson and H. K. Welsh, *Acta Crystallogr.*, **5**, 599 (1952).
33) K. Tomita, This Bulletin, **34**, 297 (1961).
34) R. F. Bryan, R. J. Poljak, and K. Tomita, *Acta Crystallogr.*, **14**, 1125 (1961).
35) C. M. Gramaccioli and R. E. Maesh, *ibid.*, **21**, 594 (1966).
36) H. Yokoi and T. Isobe, *Chem. Lett.*, **1972**, 95.
37) H. Yokoi and T. Isobe, This Bulletin, **39**, 2054 (1966); S. Antosik, N. M. D. Brown, A. A. McConnel, and A. L. Porte, *J. Chem. Soc., A*, **1969**, 545.
38) R. L. Belford, M. Calvin, and G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).
39) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York (1962).

all of them, regardless of the fact that their values of L_N, L_O, L_A, and Θ vary over considerably wide ranges, as may be seen in Tables 2 and 3. It may, accordingly, be suggested that there are certain factors which lead to almost constant differences between the g_1 and g_2 values in their crystals. The data of the X-ray analysis listed in Table 3 indicate that L_O is somewhat smaller than L_N for most of the complexes. In spite of this fact, however, the Cu–N bonding is considered to be a little more covalent than the Cu–O bonding, since the overlap integrals for the bond lengths given in Table 3 can be calculated to be larger for the Cu–N bond than for the Cu–O bond using the table of overlap integrals (we can regard the overlap integral as a measure of the degree of covalency).[40] This small difference between the two bondings in the degree of covalency, accordingly, seems to be responsible for a rhombically-distorted field around the copper atom and, therefore, for a rhombic g tensor. (Just for information, the mixing parameter, δ, in Eq. (1) could be calculated to be about 5° on the rough assumption that $\Delta E_{xy}=\Delta E_{yz}$ and $k_x^2=k_y^2$ in Eq. (2)).

[Cu(DL-Pro)$_2$]·2H$_2$O showed a complicated powder ESR line shape which was quite different from all the others, as is shown in Fig. 5; its g values also can naturally be expected to be different from the others. It can, however, be suggested from its powder ESR line shape that the powder sample of this complex may be contaminated by a significant amount of an impurity, which could not be removed by repeated recrystallizations from water. Since this sample in a frozen solution showed a typical ESR line shape due to a single complex species, as will be described below, the impurity may be considered as either a geometrical isomer of the *cis*-form or another hydrate. Interestingly, this complex has a characteristic structure of $L_N<L_O$ (contrary to the other complexes) and has the smallest θ value. The abnormal properties of the complex are also demonstrated by the powder ESR spectrum of its isomer, [Cu(L-Pro)$_2$]·2H$_2$O, whose crystal structure is yet unknown; the ESR line shape of [Cu(L-Pro)$_2$]·2H$_2$O is a so-called reverse one ($g_{/\!/}<g_\perp$, $\sin\delta=1$ in Eq. (1)), as is shown in Fig. 5. It is also an interesting fact that the ESR line shape of Cu(L-Glu)·2H$_2$O showed a normal tetragonal copper(II)-ion environment, in spite of the fact that four different coordinating groups form a planar coordination about the copper atom.[35]

Visible Absorption and Bonding Parameters. Any of the complexes employed here in both the polycrystal state and an aqueous solution showed only a single broad band in the visible region. It has been a generally accepted rule for the copper(II) complexes that the visible absorptions shift to shorter wavelengths and the g values become smaller as the copper-ligand bondings in the molecular plane become more covalent.[4,11,37,38] The mean, g_0, of the g_1, g_2, and g_3 values was plotted against the energies at the visible absorption peak, ΔE_{max}, for all the complexes under discussion; it is shown in Fig. 7. It is clear from this figure that the g_0 value decreases uniformly as the value of ΔE_{max} increases.

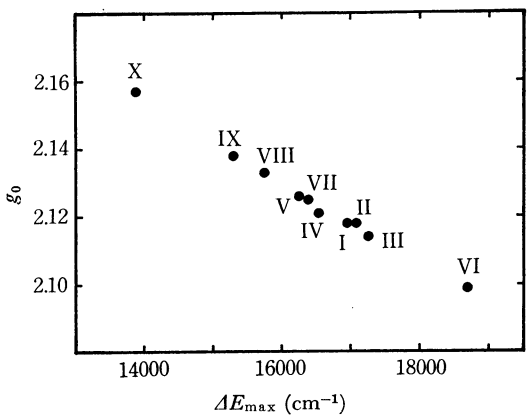

Fig. 7. A plot of g_0 against ΔE_{max} (the numbers are referred to in Table 4).

The following equation can be derived from Eq. (2):

$$k_0^2=-\frac{\Delta E_0}{4\lambda}(g_0-2)-\frac{\Delta E_0}{12\lambda}\{(e_{xz}-h_x)(g_x-2)+(e_{yz}-h_y)(g_y-2)+(e_{xy}-h_z)(g_z-2)\}+\frac{\Delta E_0}{12\lambda}\{e_{xz}h_x(g_x-2)+e_{yz}h_y(g_y-2)+e_{xy}h_z(g_z-2)\} \quad (3)$$

where $k_0^2=(1/3)(k_x^2+k_y^2+k_z^2)$ and $\Delta E_0=(1/3)(\Delta E_{xy}+\Delta E_{xz}+\Delta E_{yz})$, and where $k_s^2=k_0^2(1+h_s)$ for $s=x$, y, or z and $\Delta E_t=\Delta E_0(1+e_t)$ for $t=xy$, yz, or xz. The second and third terms on the right-hand side of Eq. (3) are much smaller than the first term. Roughly speaking, the value of (g_0-2) is inversely proportional to ΔE_0. The k_0^2 values can be regarded as a measure of the degree of covalency for the copper-ligand bondings. The approximate values of k_0^2 were calculated only from the first term, using the value of ΔE_{max} as an approximate value of ΔE_0. The k_0^2 values thus obtained, together with the values of (g_0-2) and $-4\lambda/\Delta E_{max}$, are listed in Table 4. It is shown by this table that the k_0^2 values can be arranged in the same order as that obtained in Fig. 7; the complexes become

Table 4. The values of g_0, ΔE_{max}, and k_0^2 in a polycrystalline state[a]

No.	Copper (II) complex	g_0-2	$-4\lambda/\Delta E_{max}$[b]	k_0^2
I	[Cu(L-Ala)$_2$]	0.118	0.195	0.59
II	[Cu(DL-α-NH$_2$but)$_2$]	0.118	0.194	0.60
III	[Cu(DL-Met)$_2$]	0.114	0.192	0.58
IV	[Cu(DL-Val)$_2$]	0.121	0.200	0.60
V	[Cu(DL-Ser)$_2$]	0.126	0.204	0.61
VI	[Cu(Pen)$_2$]	0.099	0.178[c]	0.55
VII	[Cu(L-Pro)$_2$]·2H$_2$O	0.125	0.202	0.61
VIII	[Cu(β-Ala)$_2$]·6H$_2$O	0.133	0.210	0.62
IX	[Cu(β-NH$_2$but)$_2$]·2H$_2$O	0.138	0.217	0.63
X	Cu(L-Glu)·2H$_2$O	0.157	0.238	0.65

a) The meanings of these parameters are described in Eq. (3).
b) $\lambda=-825$ cm^{-1}.
c) The mean of the two absorption band energies listed in Table 2 was adopted as ΔE_{max}.

40) H. H. Jaffé and G. O. Doak, *J. Chem. Phys.*, **21**, 196 (1953).

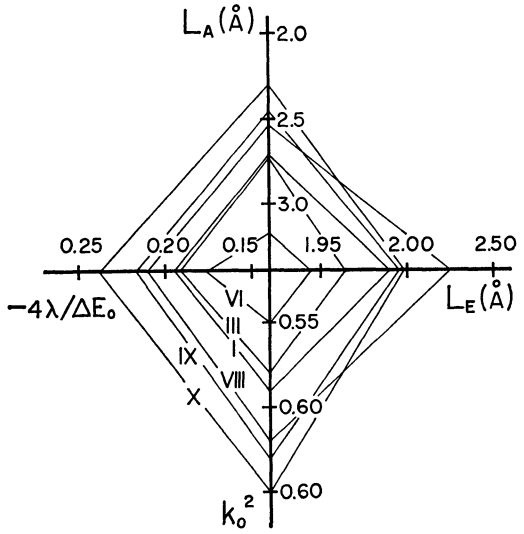

Fig. 8. A graph of L_E, L_A, k_0^2 and $-4\lambda/\Delta E_{max}$ (the numbers are referred to in Table 4).

more covalent in the copper-ligand bondings as they go to the right in Fig. 7.

It is interesting to see once more how the k_0^2 and ΔE_{max} values correlate with the actual geometry of the coordinating atoms. A plot of the values of k_0^2 and $-4\lambda/\Delta E_{max}$ and the bond lengths of L_E and L_A on the different axes is shown in Fig. 8, where $L_E=(1/2)(L_N+L_O)$, and where, for the complexes with two different L_A values, the smaller one was adopted. The meaning of this figure is as follows: as a complex has a smaller circle on this figure, the complex becomes more covalent in the coordinate bond, and there is a smaller L_E value and a larger L_A value. It is clearly shown in this figure that many circles become concentric, although there is one exception to this tendency, and the facts that the coordinate bond becomes more covalent as L_E value is smaller and the L_A value is larger may be established for this kind of complex in a crystal.

Table 5. Magnetic parameters and visible absorptions in solution[a)]

Copper (II) complex	$g_{//}$[b)]	$g_\perp$[c)]	$\lvert A_{//}\rvert$[b)] $\times 10^4 cm^{-1}$	λ_{max} (nm)
Cu(L-Ala)$_2$	2.264	2.056	178	617
Cu(DL-α-NH$_2$but)$_2$	2.265	2.056	176	614
Cu(DL-Val)$_2$	2.270	2.055	175	618
Cu(DL-Ser)$_2$	2.265	2.057	179	624
Cu(Pen)$_2$	2.258	2.057	186	612
Cu(DL-Pro)$_2$	2.266	2.058	179	610
Cu(L-Pro)$_2$	2.261	2.058	188	610
Cu(β-Ala)$_2$	2.285	2.067	139	635
Cu(β-NH$_2$but)$_2$	2.280	2.058	148	630

a) The ESR spectra were measured in aqueous–methanolic (1:1 volume ratio) solutions at 77°K, while the visible absorption spectra were measured in aqueous solution at room temperature.
b) The values were determined from the X-band ESR spectra.
c) The $g_\perp$ values were determined from the K-band ESR spectra (see Fig. 10).

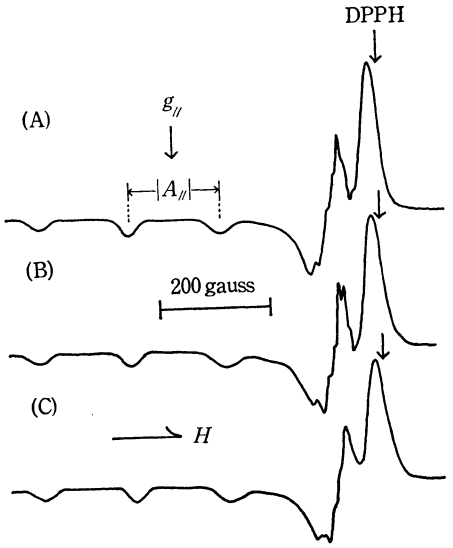

Fig. 9. X-band ESR spectra in frozen solution (at 77°K, Solvent: an equivolume mixture of water and methanol). (A):[Cu(L–Ala)$_2$], (B):[Cu(Pen)$_2$], (C):[Cu(L-Pro)$_2$]·2H$_2$O.

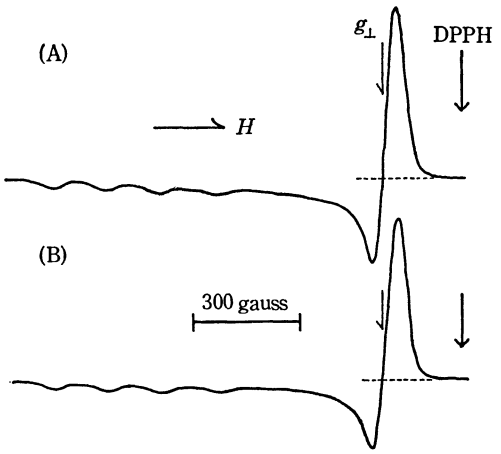

Fig. 10. K-band ESR spectra in frozen solution (at 77°K, Solvent: an equivolume mixture of water and methanol). (A):[Cu(L–Ala)$_2$], (B):[Cu(Pen)$_2$].

The Complexes in Frozen Solution. Several of the X-band and K-band ESR spectra of the complexes employed here in frozen aqueous-methanolic solutions at 77°K are shown in Figs. 9 and 10; the results are listed in Table 5. The magnetic parameters of the first seven complexes in this table were found to be almost equal to each other; $g_{//}=2.264\pm0.006$, $g_\perp=2.057\pm0.002$, and $|A_{//}|=(181\pm7)\times10^{-4}$ cm^{-1}. On the other hand, the last two complexes have somewhat larger g values and much smaller values of $|A_{//}|$ than the others.

It is characteristic of all the complexes in the solution that the observed ESR line shapes are quite similar to each other and indicate a normal elongated-tetragonal copper(II)-ion environment ($g_1\fallingdotseq g_2<g_3$), as is shown in Figs. 9 and 10; this tetragonality is clearly demonstrated, especially by the K-band ESR line shapes. This is a very interesting fact and is in contrast with the fact that the powder samples of the same com-

plexes showed a variety of ESR line shapes, with three different principal g values, as has been mentioned above. It seems, therefore, that it is a general property for the copper(II) complexes of amino acids in solution to keep the symmetry of the ligand field in a higher degree. Furthermore, this property is consistent with a previously-obtained result concerning the mixed-ligand complexes of copper(II), which also keep a high symmetry of ligand field in solution in spite of the asymmetrical coordination about the copper atom due to all the different coordinating groups.[41]

$[Cu(Pen)_2]$, whose crystals are purple, turns blue in an aqueous solution; the visible absorption spectrum of this complex shifts to a longer wavelength in the solution and resembles that of $[Cu(L\text{-}Ala)_2]$. $[Cu(Pen)_2]$ has the smallest g_3 value in a crystal, but its g_3 value becomes as large as that of $[Cu(L\text{-}Ala)_2]$ in a solution. These facts indicate that the water molecules can come close to the cupric ions in an aqueous solution for $[Cu(Pen)_2]$ as well as for $[Cu(L\text{-}Ala)_2]$, and that there is an accompanying strengthening of the axial-ligand field. Judging from the data on g and the visible absorptions, a tendency for the axial-ligand field to be strengthened in an aqueous solution can be seen in a greater or lesser degree for the anhydrous complexes. The properties of $[Cu(\beta\text{-}Ala)_2]\cdot 6H_2O$ and $[Cu(\beta\text{-}NH_2but)_2]\cdot 2H_2O$ were similar in a solution; their g values are larger than the others', and their visible absorptions appear at somewhat longer wavelengths. These two complexes, therefore, are less covalent in the coordinate bond than the others; this fact seems to be consistent with a general accepted theory that the complexes with six-membered chelate rings are less stable than those with five-membered ones.

All the facts mentioned above indicate that the copper(II) complexes of amino acids change their structures according to the molecular surroundings, and that their structures resemble each other in an aqueous solution, a normal tetragonal copper(II)-ion environment being kept.

41) H. Yokoi, M. Otagiri, and T. Isobe, This Bulletin, **44**, 2395 (1971); *ibid.*, to be published.